the ultraviolet light (hereinafter the abbreviated term UV to be appropriately used) irradiation.

Disclosure of the Invention

[0010] The first purpose of the present invention is, considering the above mentioned problem, to offer a new photocatalyst sheet in which substrates coated with fluorocarbon resin are readily weldable mutually, and also of a high antifouling property by coating the outermost surface of film/fabric structure with fluorocarbon resin containing photocatalyst and the method of manufacturing the same.

The second purpose of the present invention is, with reference to the above-mentioned problems, to offer a new photocatalyst sheet in which the uppermost surface of a substrate is coated with fluorocarbon resin layer containing a photocatalyst, said uppermost surface has water repellancy, and which has a high antifouling property when UV is irradiated on said uppermost surface, and the method of manufacturing the same.

[0011] In order to achieve the above mentioned first and second purposes, the first embodiment of the present invention is characterized in that the structure of a photocatalyst sheet of the present invention comprises: a substrate made of glass fiber; a first fluorocarbon resin layer made of PTFE coated on said substrate; a second fluorocarbon resin layer made of either one of PTFE, FEP, or PFA coated on said first fluorocarbon resin layer; and a third fluorocarbon resin layer made of FEP containing photocatalysts consisting at least of titanium oxide (TiO_2, TiO_3) coated on said second fluorocarbon resin layer, of which said photocatalysts have the part exposed on said third fluorocarbon resin layer, and the ratio of said photocatalysts in said third fluorocarbon resin layer is 10 – 60 weight %, and the surface of the fluorocarbon resin layer containing said photocatalysts of said photocatalyst sheet has water repellency upon ultraviolet light irradiation, and when photocatalyst sheets are thermally welded to each other, and if the welded part is peeled off at the rate of 20 mm/min, then whole of the fluorocarbon resin layer is completely peeled off from the substrate.

In the embodiment described above, the surface state of the substrate made of glass fiber is preferably either smooth, rough, or mesh-like. The second fluorocarbon resin layer may contain photocatalysts.

Preferably, the photoxidation ability of the surface of the fluorocarbon resin layer containing photocatalysts of a photocatalyst sheet is such that, when oleic glyceride is coated on said surface of a fluorocarbon resin layer, and ultraviolet light is irradiated onto said surface by $1mW/cm^2$, the rate of decomposition of said oleic glyceride is $0.1mg/cm^2$ day or more.

Preferably, the photoreduction ability of the surface of the fluorocarbon resin layer containing photocatalysts of a photocatalyst sheet is such that, when said photocatalyst sheet is soaked in the 0.1N (normal) silver nitrate aqueous solution, and ultraviolet light is irradiated for one minute onto the surface of said fluorocarbon resin layer containing said photocatalysts by $1mW/cm^2$, the color difference change is $\triangle E^* \geqq 1$.

The contact angle of the surface of the fluorocarbon resin layer cotaining photocatalysts is preferably about 90 degrees or more. The thickness of the fluorocarbon resin layer cotaining photocatalysts is preferably 1 μm or more.

[0012] By the embodiment described above since the melting point of FEP of the outer most layer containing the photocatalyst is lower than that of PTFE of the first fluorocarbon resin layer on the substrate made of glass fiber, the thermal welding between photocatalyst sheets is readily achieved, and the surface of the fluorocarbon resin layer containing photocatalysts contained in the uppermost layer of the photocatalyst sheet has water repellency upon ultraviolet light irradiation, and high antifouling property is given by the redox reaction when the photocatalysts exposed on the surface of the third fluorocarbon resin of the photocatalyst sheet are irradiated with the ultraviolet light involved in the sunshine.

[0013] The embodiment of the present invention is characterized by the higher melting point of the first fluorocarbon resin layer than those of the second and the third fluorocarbon resin layer, and the melting point of the second fluorocarbon resin layer higher than, or as high as, that of the third fluorocarbon resin layer. The second and the third fluorocarbon resin layers may be made of the identical resin.

The present invention is also characterized by the higher melting point of the first fluorocarbon resin layer than those of the second and the third fluorocarbon resin layers, and the melting point of the first fluorocarbon resin layer higher than, or as high as, that of the second fluorocarbon resin layer. The first and the second fluorocarbon resin layers may be made of the identical resin. The first and the third fluorocarbon resin layers may be made of the identical resin.

[0014]

[0015] In order to achieve the above mentioned first purpose, the second embodiment of the present invention is characterized in that the structure of a photocatalyst sheet of the present invention comprises: a substrate; a first fluorocarbon resin layer coated on the substrate; a second fluorocarbon resin layer coated on the first fluorocarbon resin layer; and a third fluorocarbon resin layer containing photocatalysts consisting at least of titanium oxide (TiO_2, TiO_3) coated on the second fluorocarbon resin layer, of which the third fluorocarbon resin layer has lower melting point than the first fluorocarbon resin layer, the photocatalysts have the part exposed on the third fluorocarbon resin layer, and the ratio of the photocatalysts in the third fluorocarbon resin layer is 10 – 60 weight %, and the third fluorocarbon resin layer is thermally weldable, and when photocatalyst sheets are thermally welded to each other, and if the welded part is peeled off at the rate of 20 mm/min, then whole of the fluorocarbon resin layer is completely peeled off from the substrate.

In order to achieve the above mentioned second purpose, the third embodiment of the present invention is such that the structure of a photocatalyst sheet of the present invention comprises: a substrate; a first fluorocarbon resin layer coated on the substrate; a second fluorocarbon resin layer coated on the first fluorocarbon resin layer; and a third fluorocarbon resin layer containing photocatalysts consisting at least of titanium oxide (TiO_2, TiO_3) coated on the second fluorocarbon resin layer, of which the third fluorocarbon resin layer has lower melting point than the first fluorocarbon resin layer, the photocatalysts have the part exposed on the third fluorocarbon resin layer, and the ratio of the photocatalysts in the third fluorocarbon resin layer is 10 – 60 weight %, the surface of the fluorocarbon resin layer containing photocatalysts of the photocatalyst sheet is water repellent upon ultraviolet light irradiation, and the third fluorocarbon resin layer is thermally weldable, and when photocatalyst sheets are thermally welded to each other, and if the welded part is peeled off at the rate of 20 mm/min, then whole of the fluorocarbon resin layer is completely peeled off from the substrate.

In the embodiment described above, the substrate is preferably made of glass fiber, and its surface state is either smooth, rough, or mesh-like. The first fluorocarbon resin layer is made of PTFE, the second fluorocarbon resin layer is made of either one of PTFE, FEP, or PFA, and the third fluorocarbon resin layer is made of FEP.

Preferably, the melting point of the second fluorocarbon resin layer may be as high as, or higher than, that of the third fluorocarbon resin layer. In this case, the second and the third fluorocarbon resin layers may be made of identical fluorocarbon resin.

Preferably, the melting point of the first fluorocarbon resin layer may be as high as, or higher than, that of the second fluorocarbon resin layer. In this case, the first and the second fluorocarbon resin layers may be made of identical fluorocarbon resin. Also, the second fluorocarbon resin layer may contain photocatalysts.

In order to achieve the above mentioned second purpose, the fourth embodiment of the present invention is characterized in that a photocatalyst sheet of the present invention has a substrate which is coated with fluorocarbon resin layers, at least its uppermost layer is coated with the fluorocarbon resin layer containing photocatalysts, and the surface of the fluorocarbon resin layer containing photocatalysts is water repellent upon ultraviolet light irradiation, and when photocatalyst sheets are thermally welded to each other, and if the welded part is peeled off at the rate of 20 mm/min, then whole of the fluorocarbon resin layer is completely peeled off from the substrate.

By each of the embodiments described above, the combination of the first to the third fluorocarbon resin layers, which gives excellent thermal weldability between photocatalyst sheets, can be readily obtained. Especially when a substrate is glass fiber, the first fluorocarbon resin layer is PTFE, the second fluorocarbon resin layer is either one of PTFE, FEP, or PFA, and the third fluorocarbon resin layer is FEP, since FEP as the uppermost fluorocarbon resin layer containing photocatalysts has lower melting point than PTFE as the first fluorocarbon resin layer on the substrate side, photocatalyst sheets can be easily thermally welded to each other. Also, high antifouling property is given by the redox

reaction when the photocatalysts exposed on the surface of said third fluorocarbon resin are irradiated with the ultraviolet light involved in the sunbeam. Further, the surface of the fluorocarbon resin layer containing photocatalysts of the uppermost layer of a photocatalyst sheet can be given water repellency upon ultraviolet light irradiation.

[0016] Preferably, the photoxidation ability of the surface of said fluorocarbon resin layer containing the photocatalyst is such that, when oleic glyceride is coated on said surface of fluorocarbon resin layer, and an ultraviolet light is irradiated onto said surface by 1mW/cm^2, the rate of decomposition of said oleic glyceride is 0.1mg/cm^2 day or more.

The photoreduction ability of the surface of said fluorocarbon resin layer containing the photocatalyst is such that, when said photocatalyst sheet is soaked in the 0.1N (normal) silver nitrate aqueous solution, and an ultraviolet light is irradiated for one minute onto the surface of said fluorocarbon resin layer containing the photocatalyst by 1mW/cm^2, the color difference change is preferably $\triangle E^* \geqq 1$.

The contact angle of the surface of fluorocarbon resin layer cotaining photocatalyst is preferably about 90 degrees or more.

According to the above-mentioned embodiment, when the UV light contained in the sunshine or the fluorescent light having the energy higher than the forbidden gap of the photocatalyst is irradiated onto said photocatalyst, the high antifouling property is attained by the decomposition of the organics accreted on the photocatalyst sheet surface by the redox reaction of the photocatalyst. The contact angle with water of the uppermost fluorocarbon resin layer surface of the photocatalyst sheet of the present invention can be made about 90° or more as an index of water-repellent property.

[0017] In the embodiment described above, the thickness of fluorocarbon resin layer containing the photocatalyst is 1 μ m or more. In this case since said substrate is made of fiber, and its surface has proper surface roughness, the surface area of the photocatalyst can be made larger per unit area compared with the flat and smooth surface, thereby the high antifouling property can be attained. Consequently, when the contaminant is accreted on fluorocarbon resin layer containing the photocatalyst, a high antifouling property can be attained by the redox function of the photocatalyst located in the three dimensional orientation around it owing to surface roughness. Mutual thermal weldability of the photocatalyst sheets can also be made better.

[0018] A manufacturing method of a photocatalyst sheet of the present

invention is that of a photocatalyst sheet, which comprises: a substrate made of glass fiber; a first fluorocarbon resin layer made of PTFE coated on the substrate; a second fluorocarbon resin layer made of either one of PTFE, FEP, or PFA coated on the first fluorocarbon resin layer; and a third fluorocarbon resin layer made of FEP containing photocatalysts consisting at least of titanium oxide (TiO_2, TiO_3) coated on the second fluorocarbon resin layer, of which the photocatalysts have the part exposed on the third fluorocarbon resin layer, the ratio of the photocatalysts in the third fluorocarbon resin layer is 10 – 60 weight %, and the surface of the fluorocarbon resin layer containing the photocatalysts of the photocatalyst sheet is water repellent upon ultraviolet light irradiation, and when photocatalyst sheets are thermally welded to each other, and if the welded part is peeled off at the rate of 20 mm/min, then whole of the fluorocarbon resin layer is completely peeled off from the substrate, and said method is characterized to comprise a process of coating the first fluorocarbon resin layer on the substrate, a process of coating the second fluorocarbon resin layer on the first fluorocarbon resin layer, and a process of coating the third fluorocarbon resin layer containing photocatalysts on the second fluorocarbon resin layer.

Another manufacturing method of a photocatalyst sheet of the present invention is that of a photocatalyst sheet, which is characterized to comprise: a substrate made of glass fiber; a first fluorocarbon resin layer made of PTFE coated on the substrate; a second fluorocarbon resin layer made of either one of PTFE, FEP, or PFA coated on the first fluorocarbon resin layer; and a third fluorocarbon resin layer made of FEP containing photocatalysts consisting at least of titanium oxide (TiO_2, TiO_3) coated on the second fluorocarbon resin layer, of which the photocatalysts have the part exposed on the third fluorocarbon resin layer, the ratio of the photocatalysts in the third fluorocarbon resin layer is 10 – 60 weight %, and the surface of the fluorocarbon resin layer containing said photocatalysts of the photocatalyst sheet is water repellent upon ultraviolet light irradiation, and when photocatalyst sheets are thermally welded to each other, and if the welded part is peeled off at the rate of 20

mm/min, then whole of the fluorocarbon resin layer is completely peeled off from the substrate, and said method is characterized to comprise a process of coating the first fluorocarbon resin layer on the substrate, a process of coating the second fluorocarbon resin layer containing photocatalysts on the first fluorocarbon resin layer, and a process of coating the third fluorocarbon resin layer containing photocatalysts on the second fluorocarbon resin layer.

By said method of manufacturing, coating the third fluorocarbon resin layer containing photocatalysts on the uppermost surface of the substrate makes thermal welding easy, and the photocatalysts exposed on the third fluorocarbon resin layer have water repellency upon ultraviolet light irradiation, thereby a photocatalyst sheet having antifouling property can be manufactured at low cost.

Further, in case that the second fluorocarbon resin layer contains photocatalysts, since both the second and the third fluorocarbon resin layers contain photocatalysts, a photocatalyst sheet having excellent thermal weldability and antifouling property can be manufactured.

[0019] As for the embodiment described above, the coating process of the first fluorocarbon resin layer, the second fluorocarbon resin layer either containing or not containing the photocatalyst, and the third fluorocarbon resin layer containing the photocatalyst is preferably conducted continuously. By this embodiment the photocatalyst sheet comprising the first to the third fluorocarbon resin layer continuously coated on the substrate and the third fluorocarbon resin layer containing the photocatalyst on the outermost surface may be efficiently manufactured.

[0020] As for the embodiment described above, the third fluorocarbon resin layer containing the photocatalyst may be coated on the substrate that has been coated beforehand with the first and the second fluorocarbon resin layers. By this embodiment, the manufacture of the photocatalyst sheet may be possible by first preparing the substrate coated with the first and the second fluorocarbon resin layers beforehand and by coating the third fluorocarbon resin layer containing the photocatalyst anytime later.

[0021] The coating process of the third fluorocarbon resin layer

containing the photocatalyst characteristically comprises: a coating process of the dispersion for fluorocarbon resin containing the titanium oxide fine particles as the photocatalyst on the second fluorocarbon resin